

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 403 462  
A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 90870071.9

(51) Int. Cl. 5: **C07C 5/32, C07B 35/04,  
B01J 23/22**

(22) Date of filing: 14.05.90

(30) Priority: 12.05.89 BE 8900512  
12.05.89 BE 8900513  
12.05.89 BE 8900514  
12.05.89 BE 8900515

(43) Date of publication of application:  
19.12.90 Bulletin 90/51

(84) Designated Contracting States:  
**AT BE CH DE DK ES FR GB GR IT LI LU NL SE**

(71) Applicant: **FINA RESEARCH S.A.**  
Patent Department, Zone Industrielle C  
B-6520 Feluy(BE)

(72) Inventor: **Delorme, Luc Florent Léon**  
Avenue des Petits Champs 10B  
B-1410 Waterloo(BE)  
Inventor: **Martins Mendes Cerejo, Francisco**  
Rue Plume-Coq 32  
B-7190 Ecaussines(BE)  
Inventor: **Grootjans, Jacques, François**  
Neeryresteenweg 39  
B-3061 Leefdaal(BE)

(54) **Process for the catalytic dehydrogenation of hydrocarbons.**

(57) The hydrocarbons to be dehydrogenated are contacted with a supported catalyst of the redox type wherein the metal is at a valency such that it is not in its most reduced state, and the catalyst is regenerated before being contacted with fresh feed.

**EP 0 403 462 A1**

# Process for the catalytic dehydrogenation of hydrocarbons

The present invention relates to a process for the catalytic dehydrogenation of hydrocarbons. More particularly the process of the invention uses catalytic systems of the redox type. Particularly the present invention relates to the dehydrogenation of paraffinic hydrocarbons to produce the corresponding olefinic hydrocarbons and possibly the corresponding diolefinic hydrocarbons, to the dehydrogenation of olefinic hydrocarbons to produce the corresponding diolefinic hydrocarbons, to the dehydrogenation of alkylaromatic hydrocarbons to produce the corresponding vinylaromatic hydrocarbons or to the dehydrogenation of hydrocarbons comprising at least one heteroatom.

Catalytic dehydrogenation of hydrocarbons has been carried out for many years and constitutes an important catalytic process in view of the increasing demand in dehydrogenated products which may be valorized under the most various forms such as high octane gasolines, plastic materials and synthetic rubbers.

In the field of dehydrogenation of alkylaromatic hydrocarbons, known processes include thermal dehydrogenation, catalytic dehydrogenation in the presence of an inert diluent such as steam, and oxidative dehydrogenation, the latter involving the injection of molecular oxygen in the reaction medium. However, although the oxidative dehydrogenation may have same advantages regarding reaction yield and selectivity of the desired product, it is also well known that the presence of molecular oxygen in the reaction medium leads to the formation of undesirable oxidation products such as aldehydes.

In view to partially obviate these drawbacks, it has often been proposed to use very specific catalysts having a particular selectivity towards oxidative dehydrogenation of certain hydrocarbons whether or not of the alkylaromatic type.

In this respect, it has already been proposed in US patent 4,777,319 to Kung et al. to use vanadates or molybdates of metals for the selective dehydrogenation of paraffinic hydrocarbons having from 3 to 6 carbon atoms. However, the dehydrogenation reaction is necessarily carried out in the presence of molecular oxygen, which displaces the thermodynamic equilibrium but leads to the formation of secondary oxidation products.

It has also been proposed in US 4,742,180 to Gaffney to use supported catalysts, the support being essentially an oxide of praseodymium on which there is deposited an alkaline metal having a dehydrogenating action. However, the availability of praseodymium oxide for the production of huge amounts of dehydrogenated products has to be taken into account. Moreover, it has to be noted that no significant result is indicated for the dehydrogenation of hydrocarbons. Oganowski has also proposed to use a catalyst of the  $Mg_3(VO_4)_2$  type for the dehydrogenation of ethylbenzene, but the reaction necessarily occurs in the presence of a gas containing molecular oxygen. Moreover, it is known that oxides of the  $V_2O_5$  type lead to reaction of complete combustion when used in dehydrogenation reaction of hydrocarbons carried out without bringing in molecular oxygen.

An object of the present invention is to provide an improved process for the catalytic dehydrogenation of hydrocarbons in the presence of a redox catalytic system.

An object of the present invention, is to provide an improved process for the catalytic dehydrogenation of hydrocarbons such as alkylaromatic hydrocarbons, paraffinic hydrocarbons, olefinic hydrocarbons or hydrocarbons comprising at least one heteroatom such as oxygen, nitrogen or sulfur.

Another object of the present invention is to provide an improved process for the catalytic dehydrogenation of hydrocarbons in the absence of molecular oxygen.

A further object of the present invention is to provide an improved process for the catalytic dehydrogenation of hydrocarbons in the presence of a redox catalytic system, whether or not supported, and of which one or more oxidation stages show a dehydrogenating activity.

Still a further object of the present invention is to provide a continuous process for the dehydrogenation of hydrocarbons in the presence of a redox catalytic system.

Yet another object of the present invention is to provide a redox catalyst system for a continuous process for the dehydrogenation of hydrocarbons, and a process for preparing said system.

A further object of the present invention is to provide an improved process for the dehydrogenation of hydrocarbons in the presence of a redox catalytic system comprising at least a transition metal oxide, whether or not supported, taken alone or mixed with other metals or metal oxides showing a dehydrogenation activity.

The present invention provides for a process for the catalytic dehydrogenation of hydrocarbons into corresponding dehydrogenated hydrocarbons which comprises :

- contacting the hydrocarbon feedstock to be dehydrogenated under dehydrogenation conditions, in the

absence of any gas containing molecular oxygen, with a catalyst consisting of at least one reducible oxide of a metal (I) selected from the group consisting of V, Cr, Mn, Fe, Co, Pb, Bi, Mo, U and Sn, supported on a material selected from clays, zeolitic materials of the metallo-silicate or metallo-alumino-phosphate type, and oxides of a metal (II) selected from Ti, Zr, Zn, Th, Mg, Ca, Ba, Si and Al, said catalyst having a dehydrogenation activity when said metal (I) has a valency such that it is not in its most reduced state,

- recovering the dehydrogenated hydrocarbons,
- regenerating the used catalyst, and
- contacting the regenerated catalyst with fresh hydrocarbon feedstock to be dehydrogenated.

The Applicant has now found that with the process of the invention, the presence of the molecular oxygen to perform the dehydrogenation reaction was no longer necessary, this fact constituting an important advantage over the prior processes.

According to the process of the invention, the feedstock of hydrocarbons to be dehydrogenated is contacted with a catalyst which has to fulfil several conditions. The catalyst comprises at least a reducible oxide of a metal selected from V, Cr, Mn, Fe, Co, Bi, Mo, U and Sn; reducible oxides as used herein mean the hereabove metal oxides which are reduced by contact with hydrocarbons, when operating under dehydrogenation conditions. Moreover, the metal oxide used has to have a dehydrogenating action under the reaction conditions.

Further, the Applicant has found that it is advantageous that these oxides be deposited on a support. By way of examples of suitable supports, it may be cited the oxides of metals selected from Ti, Zr, Zn, Mg, Th, Si, Ca, Ba and Al as well as clays, and zeolitic materials of the metallo-silicate or metallo-alumino-phosphate type. Within the latter type, it may be cited the alumino-silicates, the borosilicates, silico-alumino-phosphates and other analogs.

The supported catalysts used in the process of the invention may also comprise promoters such as alkali or alkaline-earth metals.

The supported catalysts may be prepared according to usual methods such as absorption, precipitation or still impregnation.

Among the various catalysts which may be used in the process of the invention, the Applicant has found that favourable results are obtained with catalysts of the vanadium oxide type deposited on a support comprising magnesium oxide.

The contact between the feedstock to be dehydrogenated and the catalyst may be performed according to different ways; for instance the catalyst particles may be used in a fixed bed, or they may be used in a fluidized bed reactor wherein said particles are circulated and thereafter recovered, what implies a suitable distribution of the particles sizes.

According to an embodiment of the process of the present invention the catalyst is placed in a fixed bed and contacted with the feedstock of hydrocarbons to be dehydrogenated, in the absence of a molecular oxygen containing gas, at a temperature comprised between about 300 and about 800°C, in order to maintain the feedstock in the vapor phase. When the activity of the catalyst is reduced over the limits which are currently acceptable, generally a reduction of about 10% of the conversion, the feedstock is no longer contacted with the catalyst, but an air stream is passed over the catalyst bed at a temperature of from about 200°C to about 1000°C in order to regenerate said catalyst under mild conditions. This regeneration comprises at least a mild oxidation of the catalyst. When the catalyst is regenerated the feedstock is again contacted with the catalyst.

According to a preferred embodiment of the present invention, the catalyst particles, whose sizes are comprised between about 0.02 and 0.3 mm, the catalyst being taken in its oxidized form, are circulating in the dehydrogenation reaction zone, and contacted with the feedstock to be dehydrogenated, in the absence of an oxygen containing gas, at a temperature comprised between about 300 and 800°C in order to maintain the feedstock in the vapor phase. The gas pressure at the outlet of the reactor is generally comprised between about  $10^5$  and  $1.3 \cdot 10^5$  Pa while residence time of the feedstock in the reactor is of about 0.5 to 15 seconds, while the residence time of the catalyst is comprised between about 0.5 second and 5 minutes; the upper limit of the residence time of the catalyst depends obviously on its activity. According to this preferred embodiment, the dehydrogenation reaction and the transportation of the catalyst to the regenerator are more particularly carried out in a fluidized bed reactor.

The catalyst in the reactor effluent is separated from the hydrocarbon effluent by suitable means. The separated catalyst is a reduced catalyst because it is in a lower oxidation state than that of the fresh catalyst which enters the reaction zone. The separated catalyst is sent to a regeneration zone where it is regenerated with gaseous stream containing molecular oxygen. This regeneration comprises at least a mild oxidation of the catalyst. The temperature in the regeneration zone is most often maintained between about 200 and about 1000°C; the residence time of the catalyst in said zone is of about 5 seconds to 5 minutes,

while that of the gas containing molecular oxygen is of about 1 to 30 seconds. The amount of gas together with the oxygen concentration must be sufficient to reoxidize the catalyst in its initial form. If this embodiment is used for the regeneration of the catalyst, then the dehydrogenation process may be carried out continuously, while it was not the case with the previous embodiment.

Among the various catalysts that may be used, the Applicant has found that favourable results are obtained, more particularly in the fluidised bed embodiment, with catalysts of the  $\text{MgO} - \text{SiO}_2 - \text{V}_2\text{O}_5$  type which may also comprise promoters such as alkali or alkaline-earth metals. These catalysts comprise 40-60 wt % (preferably about 50 %)  $\text{MgO}$ , 20-40 wt % (preferably about 30 %)  $\text{SiO}_2$ , 10-30 wt % (preferably about 15 %)  $\text{V}_2\text{O}_5$  and minor amounts of promoters (typically about 0.5 wt %  $\text{CaO}$  and about 1.5 wt %  $\text{Na}_2\text{O}$ ) and of other impurities. They are preferably prepared by spray-drying of an  $\text{MgO/SiO}_2$  suspension, followed by impregnation with an ammonium vanadate solution preferably also with a further amount of  $\text{SiO}_2$  as silicasol, evaporation and calcination at a temperature of from about  $500^\circ\text{C}$  to about  $800^\circ\text{C}$ .

The process of the invention is suitable for the dehydrogenation of alkylaromatic hydrocarbons,  $\text{C}_2 - \text{C}_{20}$  paraffinic hydrocarbons,  $\text{C}_3 - \text{C}_{20}$  olefinic hydrocarbons and hydrocarbons comprising at least one heteroatom such as oxygen, sulphur or nitrogen. Particularly, the process of the invention is applied to the catalytic dehydrogenation of ethylbenzene into styrene, of ethane into ethylene, of propane into propylene, of butane into butene, of butene into butadiene, of alcohols such as cyclohexanol into cyclohexane, or of amines into nitriles. The process is generally carried out at a temperature comprised between  $350^\circ\text{C}$  and  $800^\circ\text{C}$  and preferably between  $400^\circ\text{C}$  and  $650^\circ\text{C}$ , at a pressure comprised between 0.001 and 1 MPa, and at a hourly space velocity comprised between about 0.01 and 20.0 kg of hydrocarbon per hour and per kg of catalyst, preferably between 1 and 10.

Preferred embodiments of the invention are also described by way of the drawings according to which Figures 1 and 2 represent schematic diagrams of the reaction zone and the regeneration zone of the catalyst.

Referring now to Figure 1, which shows the dehydrogenation reaction zone 10 wherein the feedstock of hydrocarbons to be dehydrogenated enters through pipe 12 while the catalyst under its oxidized form enters through pipe 14. The dehydrogenated hydrocarbons are withdrawn through pipe 16 while the reduced catalyst is collected in the area 18 of the dehydrogenation reactor and transported to the top of the regeneration reactor 20. The gas containing molecular oxygen is introduced into pipe 22 while the reduced catalyst is introduced into pipe 24. The catalyst is recovered in the outlet pipe 14 and transported under its oxidized form in the dehydrogenation reactor 10.

Referring to Figure 2, the feedstock of hydrocarbons to be dehydrogenated enters the dehydrogenation zone 10 through pipe 12 while the catalyst under its oxidized form enters through pipe 14. The reduced catalyst is separated in the area 18 of the reactor, using e.g. a nitrogen or steam flow entering through pipe 19. The dehydrogenated feed is withdrawn through pipe 16, while the reduced catalyst is collected into pipe 24 and transported to the top of the regeneration reactor 20. Gas containing molecular oxygen is introduced into reactor 20 through pipe 22 and exits through pipe 23, while the oxidized catalyst is recovered in the outlet pipe 14 and recycled into the dehydrogenation reactor 10.

The process of the present invention shows many advantages with respect to the usual processes and particularly it enables to avoid drastically the formation of oxygenated products, due to the fact that the presence of molecular oxygen is excluded. Moreover, hydrogen is eliminated upon its formation, which enables to displace the equilibrium of the reaction and to run at less high temperatures.

Therefore, it is no more necessary to use diluents such as inert gases to displace the equilibrium; however the process of the invention may also be carried out in the presence of usual diluents.

Another non-negligible advantage of the process of the invention resides in the fact that it allows to work with quasi isothermal reactors at a less high temperature, while with the prior processes it was practically necessary to work under adiabatic conditions.

A substantial increase of the conversion and the yield in dehydrogenated hydrocarbons is also noted. Further, it has been found that it was no more necessary to work under vacuum.

The process of the invention will be better illustrated by way of the following examples.

### Example 1

#### A. Preparation of the catalyst

11.21 g of ammonium metavanadate were dissolved in 200 ml of hot deionised water.

30 g of magnesium oxide powder were homogeneized into 200 ml of water at 90 °C during 1 hour. The metavanadate solution was then added, and the resulting mixture was homogeneized at 90 °C for a further hour.

The mixture temperature was then raised to 120 °C and the excess water was evaporated during 18 hours under a nitrogen flow.

The resulting solid catalyst was calcined at 600 °C during 4 hours and pelletized. The pellets were ground and sieved to give a V<sub>2</sub>O<sub>5</sub>-type catalyst supported on magnesium oxide.

#### 10 B. Catalytic dehydrogenation of ethylbenzene

Ethylbenzene was passed in a pulse microreactor over 500 mg catalyst (as obtained from A) at a temperature of 505 °C, under atmospheric pressure, the amount of ethylbenzene being of 3.6 mg per pulse.

The following results were obtained :

- 15 - conversion of ethylbenzene : 99.1 mol %
- styrene selectivity : 91.7 mol %
- yield : 90.9 %

When the conversion was reduced by about 10% with regard to the initial conversion, ethylbenzene injections were stopped and the catalyst was regenerated by passing air in pulse mode at a temperature of 500 °C.

After regeneration, ethylbenzene injections were resumed under the same conditions, and the following results were obtained.

- conversion of ethylbenzene : 98.1 mol %
- styrene selectivity : 92.2 mol %
- 25 - yield : 90.4 %

#### C. Comparative example

30 Using adiabatic mode, a commercial catalyst for dehydrogenation of ethylbenzene, containing iron oxide, was used at a temperature of 600 °C, under a pressure of 0.06 MPa, with a liquid hourly space velocity of 0.45, and in the presence of steam in a molar ratio H<sub>2</sub>O/ethylbenzene of 8. The following results were obtained.

- conversion of ethylbenzene : 70 mol %
- 35 - styrene selectivity : 90-92 mol %
- yield : 63-64.4 %

This comparative example shows that a higher yield is obtained by the process of the invention, at lower temperatures and without having to add a diluent.

#### 40 Example 2

##### A. Catalyst preparation

45 100 g of silica powder of particle size greater than 100 mesh were calcined at 500 °C during 3 hours.

85 g of the calcined silica were impregnated under vacuum with a solution of iron nitrate prepared by dissolving 102.5 g of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in deionized water to obtain a final weight of 216 g.

After contact time of 18 hours at room temperature, the solid was filtered off and dried at 110 °C during 18 hours. The catalyst was then placed in an oven, the temperature being increased at a rate of 30 °C/h up to 600 °C and maintained at 600 °C during 10 hours.

The resulting catalyst was ground and sieved.

##### 55 B. Catalytic dehydrogenation of ethylbenzene

Ethylbenzene was passed in a pulse microreactor over 500 mg catalyst (as obtained from A) at a temperature of 505 °C, under atmospheric pressure, the amount of ethylbenzene being of 3.6 mg per pulse.

The following results were obtained :

- conversion of ethylbenzene : 98.4 mol %
- styrene selectivity : 87.2 mol %
- yield : 85.8 %

5 When the conversion was reduced by about 10% with regard to the initial conversion, ethylbenzene injections were stopped and the catalyst was regenerated by passing air in pulse mode at a temperature of 500 °C.

After regeneration, ethylbenzene injections were resumed under the same conditions, and the following results were obtained.

- 10 - conversion of ethylbenzene : 96.5 mol %
- styrene selectivity : 87.5 mol %
- yield : 84.4 %

### 16 Example 3

#### A. Preparation of the catalyst

20 Technical grade magnesium oxide (98 wt % MgO containing 0.8 wt % CaO, 0.3 wt % SiO<sub>2</sub> and 0.2 wt % Fe<sub>2</sub>O<sub>3</sub> as major impurities) was used, under the form of particles (99 % of which had a size below 0.04 mm) having a specific area of 50.9 m<sup>2</sup>/g.

4.5 kg of said oxide and 3.7 kg of silicasol (containing 40.5 wt % SiO<sub>2</sub>) were suspended in water. The suspension was spray-dried in a container kept at a temperature such that a powder was obtained having at  
25 least 70 wt % of particles between 0.04 and 0.15 mm.

The powder fraction between 0.04 and 0.15 mm was separated by sieving.

250 g of said fraction were suspended in 750 ml water. The suspension was heated to a temperature of 90 °C for 1 hour. To the hot suspension, 77.2 g silicasol (40.5 wt % SiO<sub>2</sub>) were added, then a 90 °C solution of 71.8 g ammonium metavanadate in 1400 ml water.

30 The resulting mixture was introduced into a rotating flask kept in an oil bath and homogenised at 90 °C during 15 minutes. The temperature of the oil bath was then raised to 120 °C to dry the mixture maintained at that temperature and under slight nitrogen flushing for 18 hours.

The powder then obtained was sieved to retain particles between 0.04 and 0.15 mm and placed in an oven. The oven temperature was raised at a rate of 60 °C/hour up to 600 °C and kept at that temperature  
35 for 4 hours.

A catalyst was obtained, which was sieved to retain the particles between 0.04 and 0.15 mm. It contained 15.5 wt % of vanadium (expressed as V<sub>2</sub>O<sub>5</sub>), 30 % wt % of silicon (expressed as SiO<sub>2</sub>), 1.5 wt % of sodium (expressed as Na<sub>2</sub>O), and 0.45 wt % of calcium (expressed as CaO).

The catalyst had the following physical properties :

- 40 - apparent packing density : 0.69 g/ml (ASTM D-4164-82)
- apparent bulk density : 0.58 g/ml (UOP standard method M.294-54T)
- surface area by BET technique (N<sub>2</sub> adsorption)
- calcined at 500 °C in air : 88 m<sup>2</sup>/g
- calcined at 120 °C in vacuum : 53 m<sup>2</sup>/g
- 45 - volume of pores < 100 nm : 0.27 ml/g (nitrogen desorption)
- attrition loss
- (air jet velocity of 7.07 l/min under standard conditions)
- from 0 to 5 hours : about 3.4 wt %
- from 5 to 25 hours : about 1.8 wt %

50

#### B. Catalytic dehydrogenation of ethylbenzene

55 Ethylbenzene was passed in a pulse reactor over 500 mg catalyst (as obtained from A) at a temperature of 500 °C and under atmospheric pressure, the amount of ethylbenzene being of 2 mg per pulse.

The following results were obtained :

- conversion of ethylbenzene : 97.6 mol %

- styrene selectivity : 99.4 mol %

- yield : 97.0 %

Ethylbenzene injections were continued until the conversion was reduced by about 10 % with regard to its initial value. The ethylbenzene injections were then stopped and the catalyst was regenerated by passing thereon air pulses at a temperature of 500 °C.

After regeneration, ethylbenzene injections were resumed under the same conditions, giving the following results :

- conversion of ethylbenzene : 98.8 mol %

- styrene selectivity : 98.1 mol %

- yield : 96.9 mol %

#### Example 4

A fluidized bed reactor was used, under the following temperature conditions (described by reference to Figure 2) :

- reactor (10) 500 °C

- regeneration (20) 500 °C

- stripper (18) 500 °C

- catalyst return (14) 520 °C

- feed preheater 150 °C

- feed entrance (12) 370 °C

The feed and main gases flow rates were as follows (references are to Figure 2) :

- ethylbenzene (12) 1.08 mol/h

- nitrogen at stripper (19) 2.31 mol/h

- nitrogen at regenerator (22) 34.68 mol/h

- oxygen at regenerator (22) 3.29 mol/h

The weight hourly space velocity was of 3.4.

The catalyst used was prepared as described in part A of example 3 and calcined at 550 °C immediately before use. The products (16 in Figure 2) comprised 0.57 mol/h of styrene and 0.40 mol/h of unreacted ethylbenzene, corresponding to :

- ethylbenzene conversion 63.04 mol %

- styrene selectivity 83.80 mol %

- yield 52.83 mol %

#### Examples 5 and 6

##### A. Preparation of the catalysts

The procedure described in part A. of example 1 was repeated except that 5.99 g ammonium metavanadate were dissolved in 100 ml hot deionised water (example 5) or 1.41 g in 50 ml (example 6).

##### B. Catalytic dehydrogenation of ethylbenzene

Ethylbenzene was passed in a pulse microreactor over 500 mg catalyst at a temperature of 500 °C, under atmospheric pressure, the amount of ethylbenzene being of 2.1 mg per pulse, and the contact time being of about 1.3 seconds.

The following results were obtained :

	example 5	example 6
- ethylbenzene conversion (mol %)	96.8	97.4
- styrene selectivity (mol %)	94.8	91.9
- styrene yield (mol %)	91.8	89.5

Example 7

5

Butene-1 was passed over 500 mg catalyst (as obtained from example 1 A) at a temperature of 580 ° C, under atmospheric pressure, the amount of butene-1 being of 0.95 mg per pulse.

The following results were obtained :

- conversion of butene-1 96.8 mol %
- 10 - butadiene 1,3 selectivity : 72.3 mol %
- yield : 70.0 %

When the conversion was reduced by about 10% with regard to the initial conversion, butene-1 injections were stopped and the catalyst was regenerated by passing air in pulse mode at a temperature of 500 ° C.

- 15 After regeneration, butene-1 injections were resumed under the same conditions, and the following results were obtained.

- conversion of butene-1 : 95.4 mol %
- butadiene 1,3 selectivity : 72.5 mol %
- yield : 69.1 %

20

Example 8

- 25 Propane was passed over 500 mg catalyst (as obtained from example 1 A) at a temperature of 580 ° C, under atmospheric pressure, the amount of propane being of 0.7 mg per pulse.

The following results were obtained.

- conversion of propane : 49.7 mol %
- propylene selectivity : 89.0 mol %
- yield : 42.2 %

- 30 When the conversion was reduced by about 10% with regard to the initial conversion, propane injections were stopped and the catalyst was regenerated by passing air in pulse mode at a temperature of 500 ° C.

After regeneration, propane injections were resumed under the same conditions, and the following results were obtained.

- 35 - conversion of propane : 48.2 mol %
- propylene selectivity : 89.5 mol %
- yield : 43.1 %

- 40 For comparison, a standard Pt-Sn catalyst for dehydrogenation of propane, described as catalyst A in Belgian Patent Application n° 8800157, was used at a temperature of 600 ° C, under a pressure of 0,11 MPa and with a hourly space velocity by weight of 3.

- propylene selectivity : 96.7%
- yield : 26.0%

This comparative example shows that a higher yield is obtained by the process of the invention, at lower temperatures.

45

Examples 9 and 10

- 50 The procedure of example 8 was repeated, with catalysts prepared as described in part A of example 1 except that there was used a solution of 5.99 g ammonium metavanadate in 100 ml of hot deionized water (example 9) or of 1.41 g in 50 ml (example 10). The following results were obtained :

55



	example 9	example 10
- propane conversion (mol %)	48.2	37.2
- propylene selectivity (mol %)	75.2	71.4
- yield (mol %)	36.2	26.6

**Example 11**

The procedure of example 8 was repeated, with a catalyst prepared as described in part A of example 1 except that alumina was used instead of MgO.

The following results were obtained :

- propane conversion : 68.1 mol %
- propylene selectivity : 61.3 mol %
- propylene yield : 41.7 mol %

**Claims**

1. Process for the catalytic dehydrogenation of hydrocarbons into the corresponding dehydrogenated hydrocarbons, characterized in that it comprises the steps of

- contacting the hydrocarbon feedstock to be dehydrogenated under dehydrogenation conditions, in the absence of any gas containing molecular oxygen, with a catalyst consisting of at least one reducible oxide of a metal (I) selected from the group consisting of V, Cr, Mn, Fe, Co, Pb, Bi, Mo, U and Sn, supported on a material selected from clays, zeolitic materials of the metallo-silicate or metallo-alumino-phosphate type, and oxides of a metal (II) selected from Ti, Zr, Zn, Th, Mg, Ca, Ba, Si and Al, said catalyst having a dehydrogenation activity when said metal (I) has a valency such that it is not in its most reduced state,
- recovering the dehydrogenated hydrocarbons,
- regenerating the used catalyst, and
- contacting the regenerated catalyst with fresh hydrocarbon feedstock to be dehydrogenated.

2. Process according to claim 1, characterized in that the hydrocarbons to be dehydrogenated are selected from C<sub>2</sub>-C<sub>20</sub> paraffinic hydrocarbons, C<sub>3</sub>-C<sub>20</sub> olefinic hydrocarbons and mixtures thereof.

3. Process according to claim 1, characterized in that alkylaromatic hydrocarbons are dehydrogenated into the corresponding vinylaromatic hydrocarbons.

4. Process according to claim 1, characterized in that the hydrocarbons to be dehydrogenated are selected from hydrocarbons containing at least one heteroatom such as oxygen, sulfur or nitrogen.

5. Process according to either of claims 1 to 4, characterized in that a catalyst comprising of at least a vanadium oxide or an iron oxide is used.

6. Process according to either of claims 1 to 5, characterized in that the catalyst is supported on magnesium oxide or on zinc oxide.

7. Process according to any one of claims 1 to 5, characterized in that the catalyst is supported on a zeolitic material selected from alumino-silicates, borosilicates and silico-alumino-phosphates.

8. Process according to any one of claims 1 to 7, characterized in that the dehydrogenation of alkylaromatic hydrocarbons and the recovery of the catalyst are carried out in a fluidized bed reactor.

9. Process according to any one of claims 1 to 8, wherein the catalyst recovered from the dehydrogenation reactor is regenerated by sending it into a second reactor wherein a gaseous flow is passed at a temperature of from 200 to 1000 °C, with a residence time of from 5 seconds to 5 minutes, and recovered for recycling to the dehydrogenation reactor.

10. Process according to claim 9, wherein the second reactor is of the fluidized bed type and the gaseous flow contains molecular oxygen.

11. Process according to any one of claims 1 to 7, characterized in that the supported catalyst is regenerated by passing on the catalyst bed a gaseous flow containing molecular oxygen at a temperature of from 200 to 1000 °C.

12. Process according to claim 11, wherein the catalyst is regenerated when a reduction of about 10% of the conversion of hydrocarbons is observed.

13. Process according to any one of claims 1 to 12, characterized in that the dehydrogenation reaction is carried out, in the absence of gas containing molecular oxygen, at a temperature of from 360 to 800 °C, preferably between 400 and 650 °C, at a pressure of from 0.001 to 1 MPa, and with an hourly spatial velocity comprised between 0.01 and 20 kg of hydrocarbon per hour and per kg of catalyst.

5 14. Process according to any one of claims 1 to 13, wherein the catalyst is of the MgO - SiO<sub>2</sub> - V<sub>2</sub>O<sub>5</sub> type.

15. Process according to any one of claims 1 to 14, wherein the catalyst comprises from 40 to 60 wt % of MgO, from 20 to 40 wt % of SiO<sub>2</sub>, from 10 to 30 wt % of V<sub>2</sub>O<sub>5</sub>, and minor amounts of promoters and of other impurities.

10 16. Process according to claim 15, wherein the catalyst comprises about 50 wt % MgO, about 30 wt % SiO<sub>2</sub>, about 15 wt % of V<sub>2</sub>O<sub>5</sub>, and minor amounts of promoters and of other impurities.

17. Process according to either of claims 15 and 16, wherein the catalyst is prepared by spray-drying of an MgO/SiO<sub>2</sub> suspension, followed by impregnation with an ammonium vanadate solution preferably also with a further amount of silica as silicasol, evaporation and calcination at a temperature of from 500 °C to 800 °C.

20

25

30

35

40

45

50

55

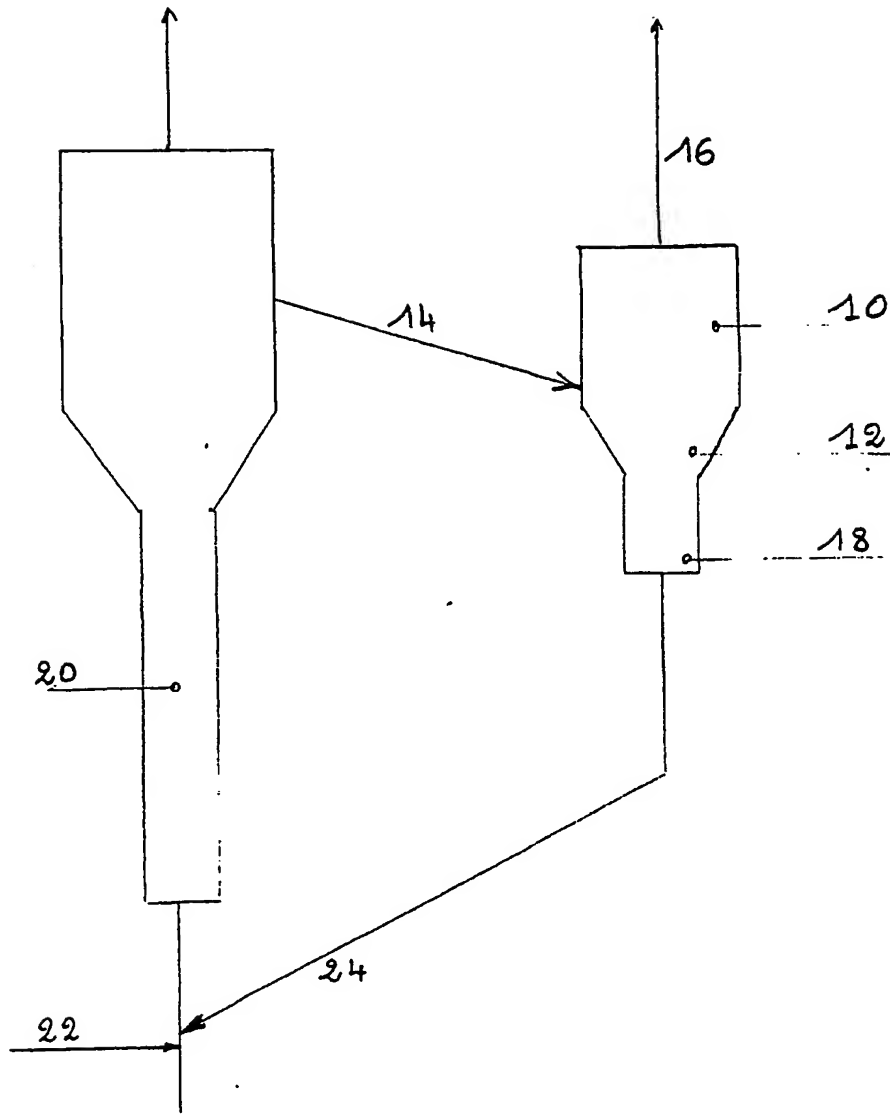
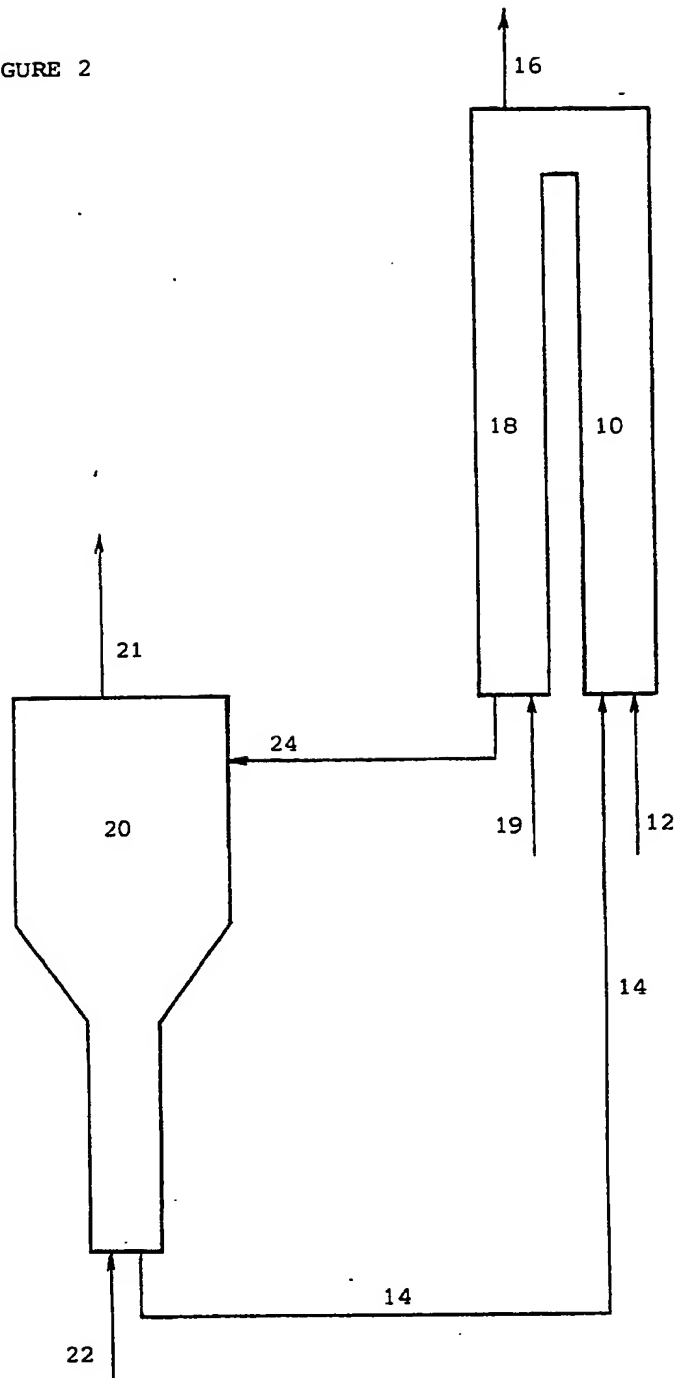


Figure 1

FIGURE 2





European Patent  
Office

**PARTIAL EUROPEAN SEARCH REPORT**  
which under Rule 45 of the European Patent Convention  
shall be considered, for the purposes of subsequent  
proceedings, as the European search report

Application number

EP 90 87 0071

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-3 118 007 (W. KRÖNING et al.)  * Claims *  --	1-2, 5,8, 13	C 07 C 5/32 C 07 B 35/04 B 01 J 23/22
X	GB-A- 840 082 (DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ)  * Claims *  --	1-2,5	
X	US-A-4 607 129 (LEE)  * Claims *  --	1-2,5	
X	US-A-4 644 089 (LEE)  * Claims *  --	1-2,5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 C 5/00 C 07 B 35/00
<b>INCOMPLETE SEARCH</b>			
<p>The Search Division considers that the present European patent application does not comply with the provisions of the European Patent Convention to such an extent that it is not possible to carry out a meaningful search into the state of the art on the basis of some of the claims.</p> <p>Claims searched completely: 1-3 Claims searched incompletely: 5-17 Claims not searched: 4 Reason for the limitation of the search:</p> <p>The hydrocarbons containing heteroatoms are not defined, hence a meaningful search is impossible.</p> <p>Claims 5-17 searched in far as related to claims.</p>			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>14-08-1990</b>	Examiner <b>VAN GEYT</b>
<b>CATEGORY OF CITED DOCUMENTS</b>		<b>T : theory or principle underlying the invention</b> <b>E : earlier patent document, but published on, or after the filing date</b> <b>D : document cited in the application</b> <b>L : document cited for other reasons</b>	
<b>X : particularly relevant if taken alone</b> <b>Y : particularly relevant if combined with another document of the same category</b> <b>A : technological background</b> <b>O : non-written disclosure</b> <b>P : intermediate document</b>		<b>&amp; : member of the same patent family, corresponding document</b>	



European Patent  
Office

# PARTIAL EUROPEAN SEARCH REPORT

Application number

EP 90 87 0071

-2-

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	FR-A- 827 068 (UNIVERSAL OIL PRODUCTS)  -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)